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INFORMATION FROM  
FOREIGN DOCUMENTS OR RADIO BROADCASTS

REPORT

CD NO.

COUNTRY USSR

SUBJECT Scientific - Chemistry

HOW PUBLISHED Periodical

WHERE PUBLISHED Moscow

DATE PUBLISHED 11 March 1948

LANGUAGE Russian

DATE OF INFORMATION 1948

DATE DIST. 8 Apr 1949

NO. OF PAGES 4

SUPPLEMENT TO REPORT NO.

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SOURCE Doklady Akademii Nauk SSSR, Novaya Seriya, Vol LIX, No 8, pp 43-46, 1948.  
(FIB Per Abs 47117 -- Translation requested.)

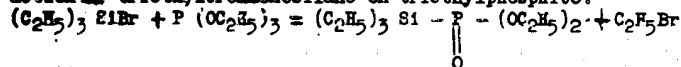
SILICON-PHOSPHORUS ORGANIC COMPOUNDS

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It was pointed out in previous papers (1) that it is possible to obtain a new type of organic phosphorus derivatives containing a direct phosphorus-silicon bond by the action of organic halogen compounds on the full esters of phosphorous acid, using A. Ye. Arbuzov's reaction.

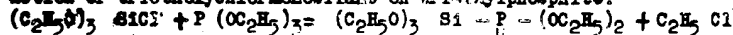
In the course of this work we studied the reactions of triethylphosphite with halogen-silicon organic derivatives. This led to the preparation of compounds with a phosphorus-silicon bond.

The diethyl ether of triethylphosphonmonosilane was prepared by the action of triethylbromosilane on triethylphosphite.



NOTE: As in the case of triphenylbromotin and triphenylbromolead, when triphenylchlorosilane reacts with triethylphosphite the phosphorus-silicon derivative is not formed, but disproportionation of triphenylchlorosilane occurs, leading to the formation of tetraphenylmonosilane.

The diethyl ether of triethoxyphosphonmonosilane was prepared by the action of triethoxychlorosilane on triethylphosphite.



The latter reaction is accompanied by the formation of considerable quantities of tetraethoxysilane.

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The reaction between triethoxychlormonosilane and sodium diethylphosphite leads to the formation of the same products: the diethyl ether of triethoxyphosphonmonosilane and tetraethoxymonosilane.

[Words underlined may be incorrect, due to omission of some letters in Russian text.]

The formation of tetraethoxymonosilane in the reactions of triethoxychlormonosilane with sodium diethylphosphite and triethylphosphite is most easily explained by the disproportionation of triethoxychlorosilane under the influence of temperature which was observed by Yu. N. Vol'nov (2).

However, the formation of tetraethoxymonosilane occurs during the sodium diethylphosphite reaction at low temperature in an ether medium.

Moreover, we did not observe disproportionation of triethoxychlormonosilane even when heated to 200°C for 6 hours in a sealed tube, or when boiled with a reflux condenser in the absence of atmospheric moisture for 7 hours (see also (5)). The conditions under which disproportionation of triethoxychlormonosilane occurs should, therefore, be specified more accurately.

We showed (1) that in the case of tin-phosphorus organic compounds the P-Sn link, stable at high temperatures, is severed by the action of chlorine, halogen-hydrogen acids, and acetyl chloride.

A study of the strength of the Si-P link as exemplified in the compounds prepared by us showed that this link also is unstable. For example, the diethyl ether of triethoxyphosphonmonosilane readily decomposes on direct heating to 200°, tetraethoxymonosilane being formed (yield over 70 percent).

It is probable that the preparation of tetraethoxymonosilane by the reaction of triethoxychlormonosilane with triethylphosphite or sodium diethylphosphite is also explained by this decomposition of the diethyl ether of triethoxyphosphonmonosilane. The Si-P bond in the diethyl ether of triethoxyphosphonmonosilane is very easily broken by the action of chlorine at room temperature.

The reaction proceeds according to the equation

$$(C_2H_5O)_3Si - \underset{\text{O}}{\underset{|}{P}} - (OC_2H_5)_2 + Cl_2 = (C_2H_5O)_3SiCl + Cl - \underset{\text{O}}{\underset{|}{P}} - (OC_2H_5)_2$$

Triethoxychlormonosilane and the chloranhydride of diethylphosphoric acid were isolated from the reaction products. The latter was identified by preparing the anilide with MP 95° (3) as well as by comparing physical constants.

#### EXPERIMENTS

##### Diethyl Ether of Phosphotriethylmonosilane

Ten gm of triethylbromosilane with BP 161-162° (4) and 8.5 gm of triethylphosphite were heated in a Wurtz flask on a water bath. Reaction began at 70°C, accompanied by evaporation of ethyl bromide, when 5.1 gm of ethyl bromide were evaporated (theory 5.5 gm). Fractional distillation of the reaction product yielded 1.2 gm triethylphosphite, 0.7 gm diethylphosphoric acid (BP 71-74°/11 mm), 5.0 gm of fraction 104-125°/13 mm and 4 gm of the diethyl ether of phosphotriethylmonosilane as a colorless liquid with BP 158-159°/10 mm;  $n_D^{20}$  1.4390,  $d_4^{20}$  0.9659. 0.1188 gm of substance: 0.2066 gm CO<sub>2</sub>; 0.1056 gm H<sub>2</sub>O.

Obtained %: C 47.43; H 9.87.  
C<sub>10</sub>H<sub>25</sub>O<sub>3</sub> PSi. Calculated %: C 47.61; H 9.92.

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**CONFIDENTIAL**Diethyl Ether of Phosphontriethoxymonosilane

Twenty gm triethoxychloromonsilane BP 157-158° and 16 gm triethylphosphite were heated to 120-130°. Violent evolution of ethyl chloride occurred (30 min). Fractional distillation of the reaction product gave the fractions: 38-46°/5 mm - 15 gm, 52-82°/3 mm - 2.3 gm, 82-86°/3 mm - 5.2 gm, and 125-160°/3 mm - 6.3 gm.

Twelve gm tetraethoxymonosilane BP 62-64°/14 mm,  $n_D^{20}$  1.3850, and 2.1 gm diethylphosphoric acid BP 75-76°/14 mm,  $n_D^{20}$  1.4085 were isolated from the first fractions, while 5.8 gm of the diethyl ether of triethoxyphosphonmonosilane BP 113°/12 mm,  $n_D^{20}$  1.4080,  $d_4^{20}$  0.9282 were isolated from the later fractions.

0.1028 gm substance: 0.1500 gm CO<sub>2</sub>; 0.0766 gm H<sub>2</sub>O

Obtained %: C 39.80; H 8.28.

C<sub>10</sub>H<sub>25</sub>O<sub>5</sub> PSi Calculated %: C 40.00; H 8.33.

Fifteen gm triethoxychlorosilane was gradually added to a solution of sodium diethylphosphite (from 10.8 gm diethylphosphoric acid and 2 gm sodium) in 50 cc ether. Reaction proceeds with considerable evolution of heat. The whole is then heated for 3 hours in a water bath. After decanting ether from sodium chloride, evaporation of the ether and fractional distillation of the residue, 7.8 gm tetraethoxymonosilane BP 62°/14 mm and 3.5 gm of the diethyl ether of triethoxyphosphonmonosilane BP 114°/12 mm,  $n_D^{20}$  1.4075 were obtained.

The diethyl ether of triethoxyphosphonmonosilane (6 gm) was heated at 200° for 2-3 minutes and then evaporated from the small flask with Vidmer (?) dephlegmator in vacuo. Three gm of tetraethoxymonosilane BP 60-61°/12 mm,  $n_D^{20}$  1.3860 was obtained.

0.0958 gm substance: 0.1598 gm CO<sub>2</sub>; 0.0830 gm H<sub>2</sub>O.

Obtained %: C, 45.50; H 9.62 and 3 gm residue boiling in limit 65-140°/6 mm. C<sub>8</sub>H<sub>20</sub>O<sub>4</sub> Si. Calculated %: C 46.16; H 9.61.

A 3-percent solution of chlorine in chloroform (2 gm chlorine) was added to a solution of 8 gm diethyl ether of triethoxyphosphonmonosilane in 40 cc of chloroform. The solution became colorless after standing for 12 hours at room temperature. On fractional distillation, 2.8 gm of 66-70°/18 mm fraction and 4 gm of 85-100°/18 mm fraction were obtained. Obtained 1.9 gm triethoxychloromonsilane BP 157-159° from first fraction. Obtained 3.1 gm chloranhydride of diethylphosphoric acid BP 96-99°/23 mm,  $n_D^{20}$  1.4110 from second fraction. MP of anilide 95°. Sample mixed with anilide of diethylphosphoric acid (3) MP 94-95°.

Action of Triphenylchlorosilane on Triethylphosphite

Four gm triphenylchlorosilane and 4 gm triethylphosphite were heated for 4 hours at 160°. On cooling, crystals of tetraphenylsilane were deposited. The greater part of the products returned to their previous state.

Action of Temperature on Triethoxychlorosilane

Fifteen gm of triethoxysilane BP 157-158° were heated in a closed tube at 200° for 6 hours. Obtained 14.1 gm of original chloride. Residue 0.5 gm 38 gm triethoxychlorosilane was heated with reflux condenser (calcium chloride tube) for 7 hours. Obtained 35.6 gm of original chloride. Residue with BP above 160° was 2 gm.

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Submitted 3 January 1948

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